Enhancing the Atomic-level Understanding of CO_2 Mineral Sequestration Mechanisms *via* Advanced Computational Modeling

Andrew V.G. Chizmeshya [1,2], Deirdre Gormley [2], Michael Kocher,
Michael J. McKelvy [1,2] and George H. Wolf [3]

[1] *Center for Solid State Science, Arizona State University, Tempe AZ*
[2] *Science and Engineering of Materials Ph.D. Program, Arizona State University, Tempe AZ*
[3] *Department of Chemistry and Biochemistry, Arizona State University, Tempe AZ*

CSSS:	Michael J. McKelvy Andrew V.G. Chizmeshya Ray W. Carpenter Renu Sharma	**Chem/Biochem:** **Physics/Astronomy:**	George H. Wolf Otto F. Sankey
SEM Graduate Program:	Deirdre Gormley Ryan Munez	**Post-doctoral associates:**	Jason Diefenbacher Hamdallah Bearat
		Undergrad assistant:	Michael Kocher

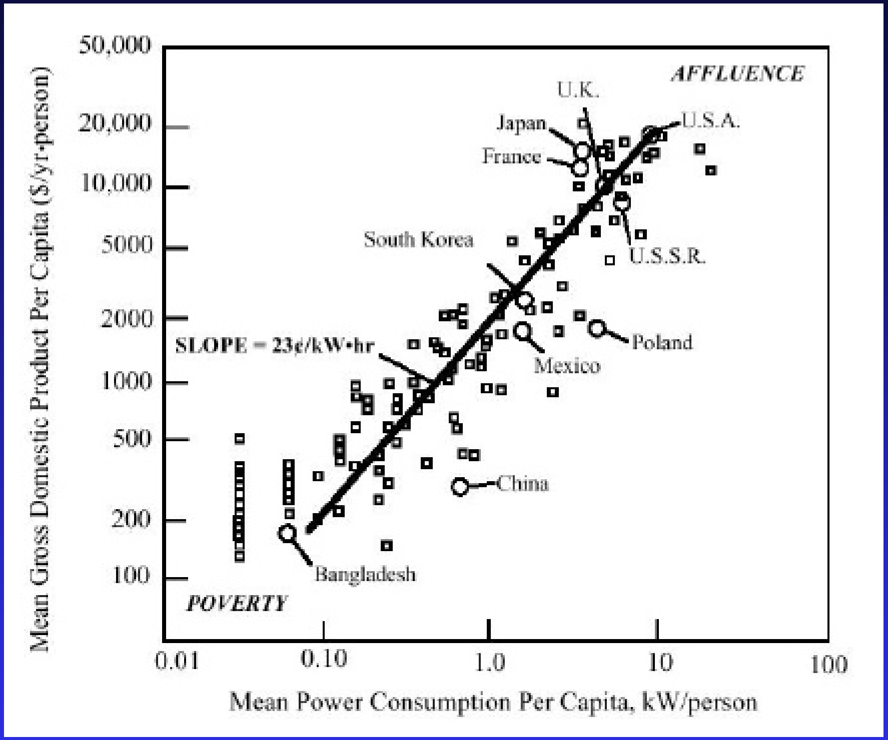
This research is supported by DOE Fossil Energy Advanced Research managed by the National Energy Technology Laboratory under:

UCR Grant DE-FG26-01NT41295 **NETL/ANL Contract 1F-01262**

& Pittsburgh Supercomputer Center grant

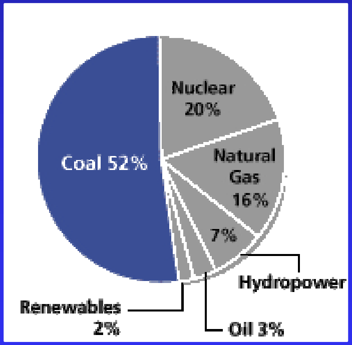
MPS030002P

World Needs Low Cost Energy



Fossil Energy
contributes 80-90%
of the total World Energy.

Cannot eliminate the
biggest resource from
the world market.



10 billion people trying to consume energy as US citizens do today would raise energy demand 10 fold

The Greenhouse Gas Problem

Human activities are causing worldwide CO_2 levels to rise

World: 22Gt/year US: 25t/person/year

Climate Change:

- CO_2 is a greenhouse gas

Nitrogen (N_2), 79%
Oxygen (O_2), 21%

Water vapor (H_2O), 0.1%
Carbon Dioxide (CO_2), 0.03%
Methane (CH_4), 0.0001%
Nitrous Oxide (NO_2), 0.00003%

Direct Ecological Effects:

- CO_2 acidifies the soil
- CO_2 is physiologically important
- Global warming:
  - Doubling CO_2 concentration?
  - Estimates vary ~ 0.4 - 4.5 C
- Melting of ice caps → sea level

…to cope with uncertainty one usually buys insurance *(K. Lackner, 2002)*

CO_2 Mineral Sequestration…

The ground state energy of carbon is a mineral carbonate

- Permanent: - stable on geologic time scales
  - no legacy issues

- Environmentally benign

- Mg-rich mineral feedstock available in large quantities worldwide…

CO_2 Mineral Sequestration…

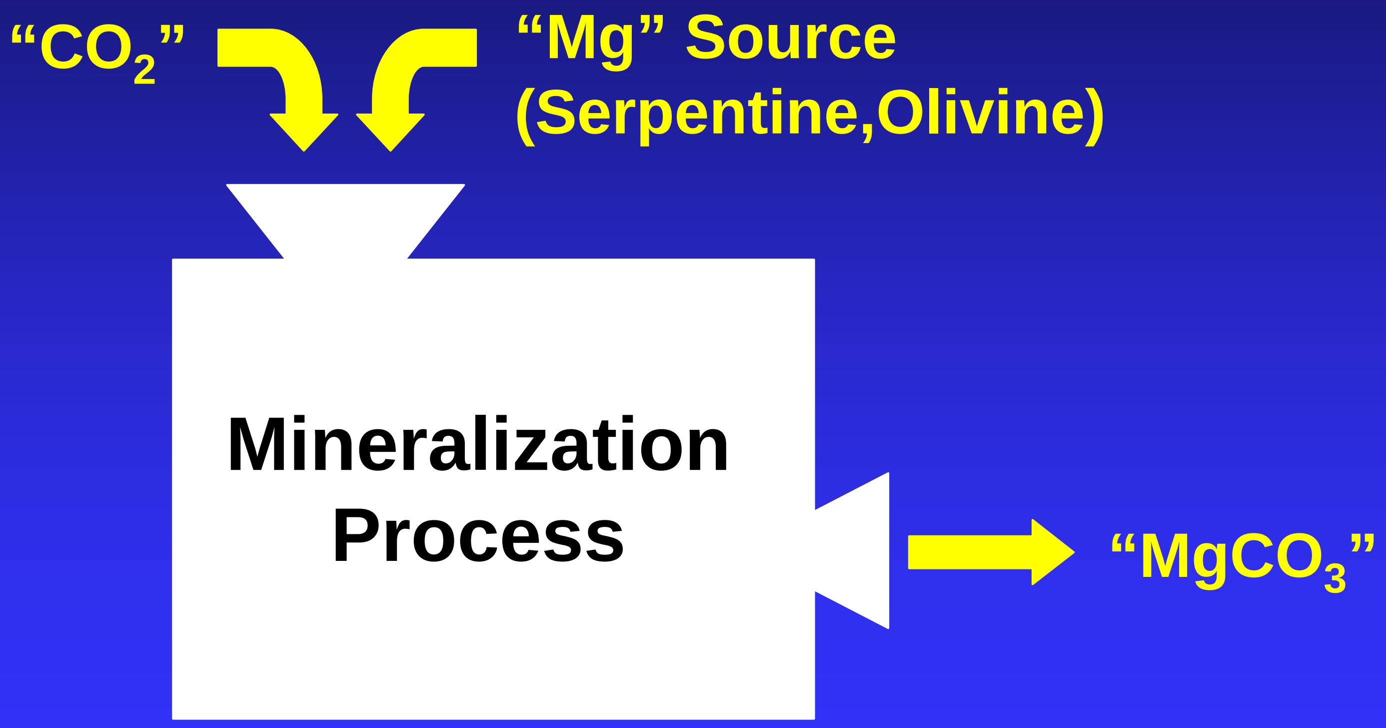
The ground state energy of <u>carbon</u> is a <u>mineral carbonate</u>

http://www.fe.doe.gov/techline/tl_arc_sequestration.shtml

"Magnesite" - $MgCO_3$

CO_2 Mineral Sequestration…

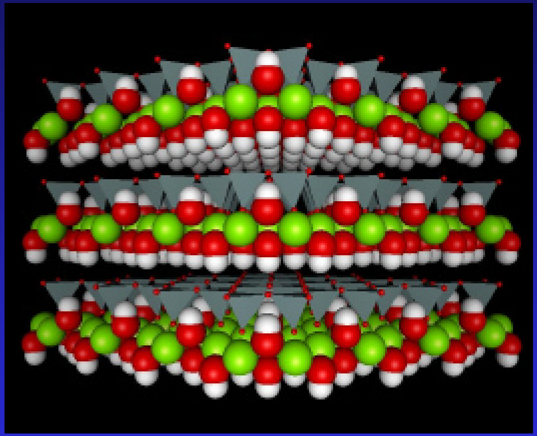
The ground state energy of carbon is a mineral carbonate



Mineral Carbonation Reactions

Generalized reaction:

- $(Mg, Ca)_xSi_yO_{x+2y+z}H_{2z} + xCO_2 \rightarrow x(Mg,Ca)CO_3 + ySiO_2 + zH_2O$



Serpentine:

$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$

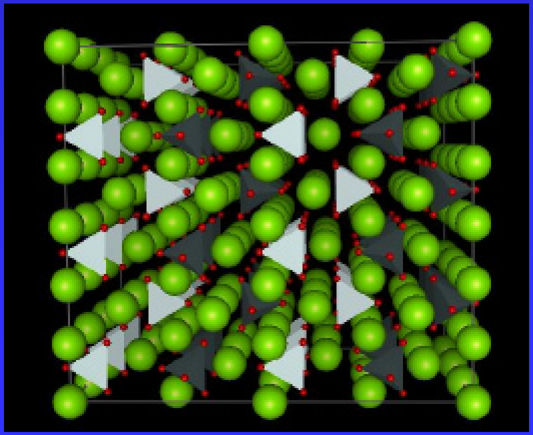
MgO: 38-45 wt %

Iron oxides: 5-8 wt %

Water: 13 wt %

Exothermic reaction: **+64 kJ/mole**

One ton to dispose of 1/2 ton of CO_2



Olivine (Primarily forsterite):

$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2$

MgO: 45-50 wt %

Iron oxides: 6-10 wt %

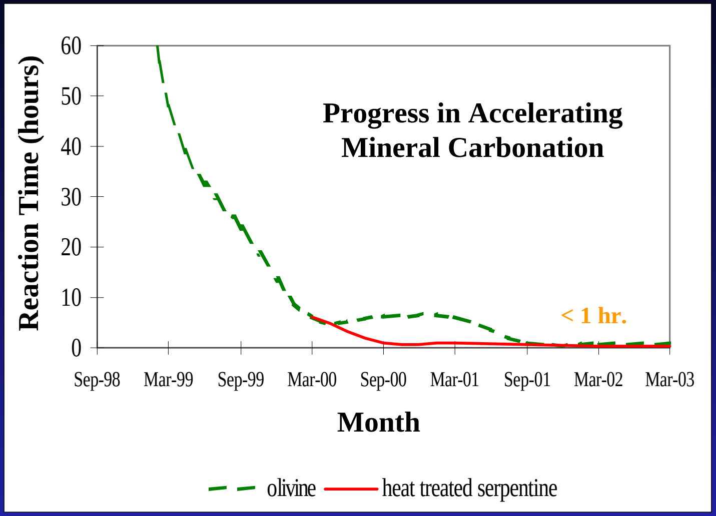
Exothermic reaction: **+95 kJ/mole**

One ton to dispose of 2/3 ton of CO_2

THE CARBON DIOXIDE MINERAL SEQUESTRATION WORKING GROUP

- Albany Research Center
- Arizona State University
- Los Alamos National Laboratory
- National Energy Technology Laboratory
- Science Applications International Corporation
- University of Utah
- Pennsylvania State University

PROGRESS…



Use aqueous solution → add sodium bicarbonate and NaCl:

Sodium bicarbonate increases HCO_3^- concentration

NaCl may help release Mg ions from silicate

Albany Research Center:
78% conversion can be achieved in 30 minutes at 185 bar, & 155 ^{0}C

- Heat pre-treatment (600-650^{o}C) of serpentine removes chemically-bonded water and creates "open" structure…
- Various types of mechanical attrition improve reaction in olivine feedstock…
- Pretreament is energy intensive!

GOAL: Improve of carbonation reaction rate in serpentine and olivine feedstock. Reduce process cost.

APPROACH: Thermal, mechanical or chemical *beneficitation*

OVERVIEW OF ASU SIMULATION & MODELING EFFORTS

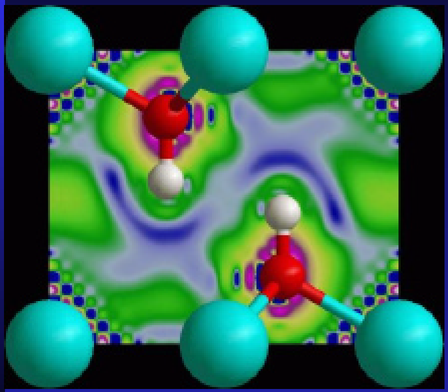
Lizardite:	**Structural and Vibrational models of 50% de-hydroxylated Lizardite**
	Decomposition mechanism in 12.5% dehydroxylated material -- Simulation of "Differential XRD"
	Quantum Molecular Dynamics Simulation of Dehydroxylation
Forsterite/Olivine:	**Surface reconstruction of Forsterite/Olivine Surfaces**
	Dissolution Reactions in Olivine
Solution Reactions:	**Quantum Molecular Dynamics of Solutions**
	Approximate Quantum-based methods
Carbonate Product:	**Oxidation stability of (Mg,Fe)CO_3**
Spectroscopy:	**Simulation of EELS, Raman, FTIR, EXAFS and XRD spectra**

SIMULATION AND MODELING GOAL

Emphasis on complementarity with ongoing experimental studies

Ab Initio Electronic Structure Methods:

VASP(PWPP), WIEN2K (FPLAPW), MDG (PM3-QMD Cluster code)



State-of-the-Art Simulation methods:

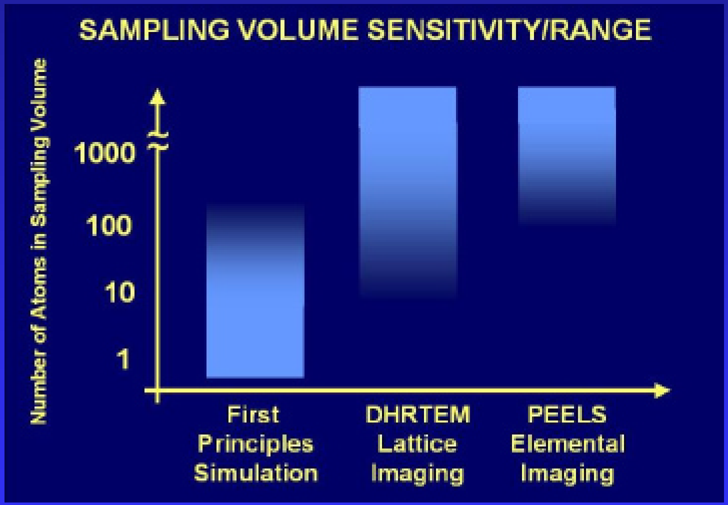
- Based on a modern Density Functional Theory description of atomic, molecular and condensed matter system.
- No assumptions are made concerning “bonding”. There are only electrons and nucleii. The full many-electron problem is solved numerically to predict the forces and subsequent motion of the ions/atoms.

Advanced Simulation and Modeling:

Use modern “first principles” methods to simulate systems of interest at the atomic and nano scale – complementary approach to experimental atomic-level probes.

Can directly simulate energetic, electronic, vibrational and structural properties of the solids, liquids and gases.

CHEMISTRY: Examine reactions at surfaces (interaction of CO_2/H_2O with minerals) – activation barriers, adsorption energies, bonding structure, adsorption geometry. Elucidate initial stages of dehydroxylation and carbonation.



Simulate the response of the systems to experimental probes, e.g., predict ELNES, EELS, XPS, EXAFS, Raman, IR spectra. Compare with experiment to aid interpretation.

Solid Phases

Properties of Solid Phases

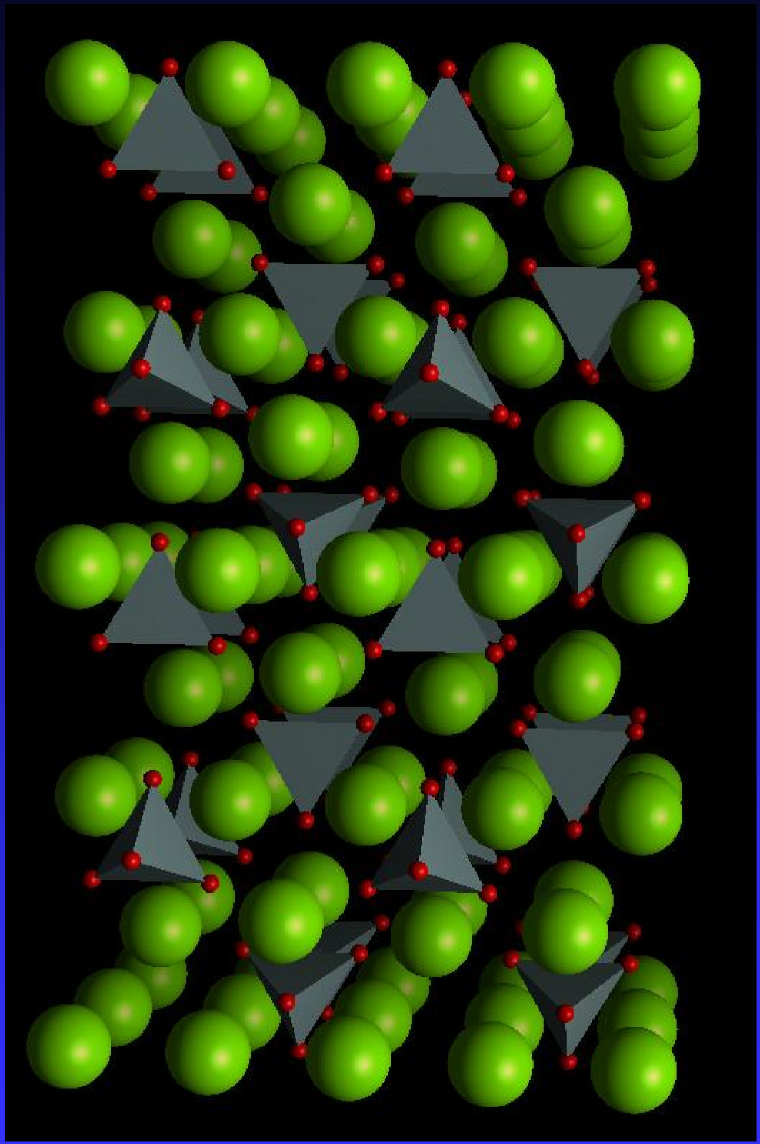
Solid Reactants: Forsterite, Olivine, Lizardite, Meta-lizardite

Solid Products: Magnetite, "carbonate" $(Mg_x,Fe_{1-x})CO_3$, silica, others?

- *Equations of state:* External stress, Heating → Apart from dehydroxylation, stable over {P,T} range in experiments (small α, large K)
- *Energy changes* associated with structural/chemical modifications are of interest: Defect energies, Solid solutions $(Mg,Fe)_2SiO_4$, $(Mg,Fe)CO_3$
- *Spectroscopic signatures:* Given a predicted ground state structure use first principles methods to predict XRD, FTIR/Raman, EELS and HRTEM spectra of <u>solids</u>.

Forsterite Mg_2SiO_4

Volume (Å^3)	295.16	**290.30**
a(Å)	4.79	**4.76**
b(Å)	10.27	**10.21**
c(Å)	6.00	**5.98**
α	90	**90**
β	90	**90**
γ	90	**90**
Z	4	
ΔE_0 (eV)	-193.6594	
$\Delta E_0/Z$ (eV)	-48.4149	



Analysis of electronic structure suggests: "ionic" lattice: M_2X

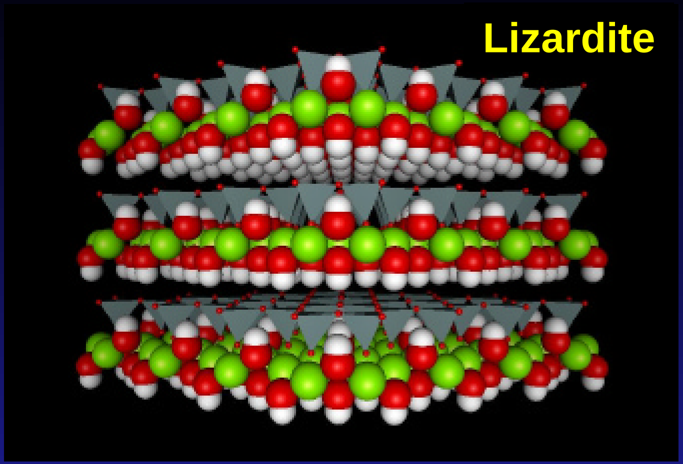
$M = Mg^{2+}$

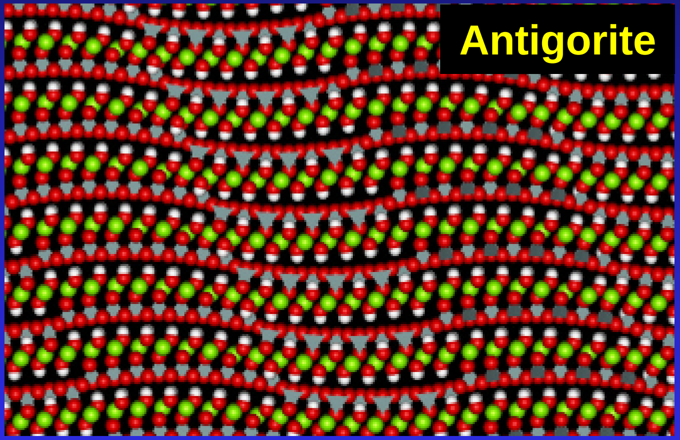
$X = SiO_4^{4-}$

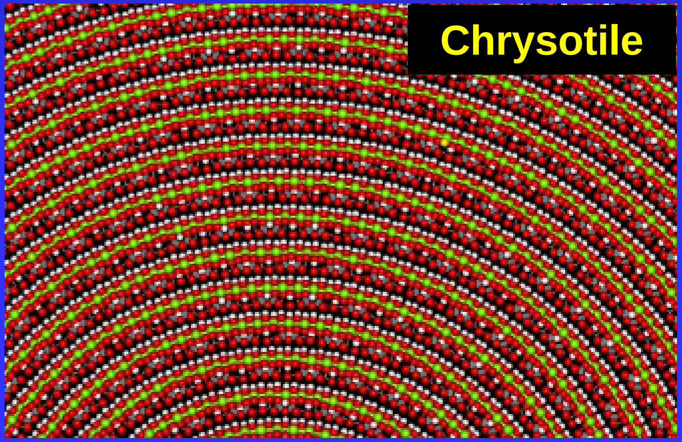
Lizardite	$Mg_3Si_2O_5(OH)_4$	
Volume (Å^3)	184.76	**179.35**
a(Å)	5.36	**5.33**
b(Å)	5.36	**5.33**
c(Å)	7.42	**7.29**
α	90	**90**
β	90	**90**
γ	120	**120**
Z	1	
ΔE_0 (eV)	-114.9601	
$\Delta E_0/Z$ (eV)	-114.9601	

Analysis of electronic structure suggests:

- “ionic” MgO-like sheets
- covalent hydroxyl & SiO_4 units







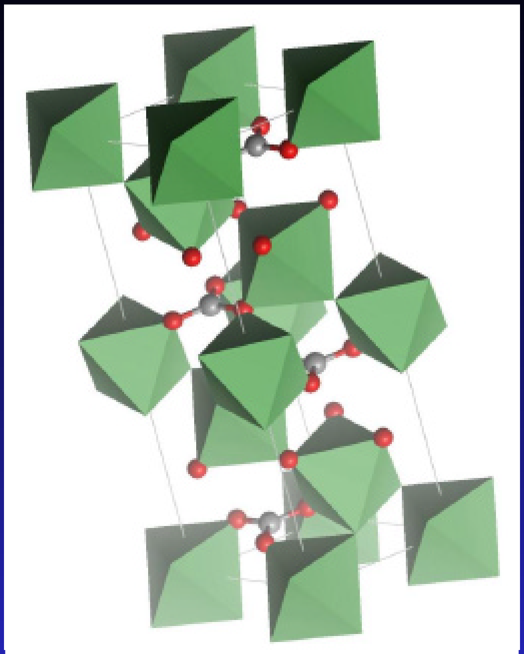
Magnesite $MgCO_3$

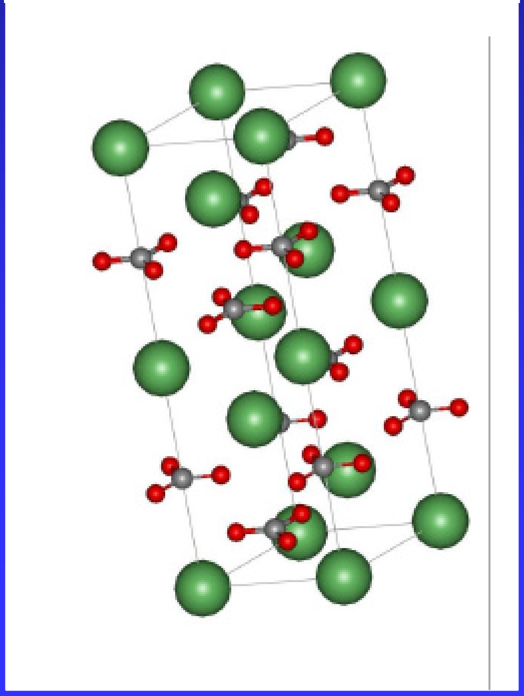
Volume (Å^3)	279.60	**279.52**
a(Å)	4.68	**4.63**
b(Å)	4.68	**4.63**
c(Å)	15.06	**15.02**
α	90	**90**
β	90	**90**
γ	120	**120**
Z	6	
ΔE_0 (eV)	-213.2506	
$\Delta E_0/Z$ (eV)	-35.5418	

Analysis of electronic structure & vibrational spectrum suggests: "ionic" lattice: MX

$M = Mg^{2+}$

$X = CO_3^{2-}$





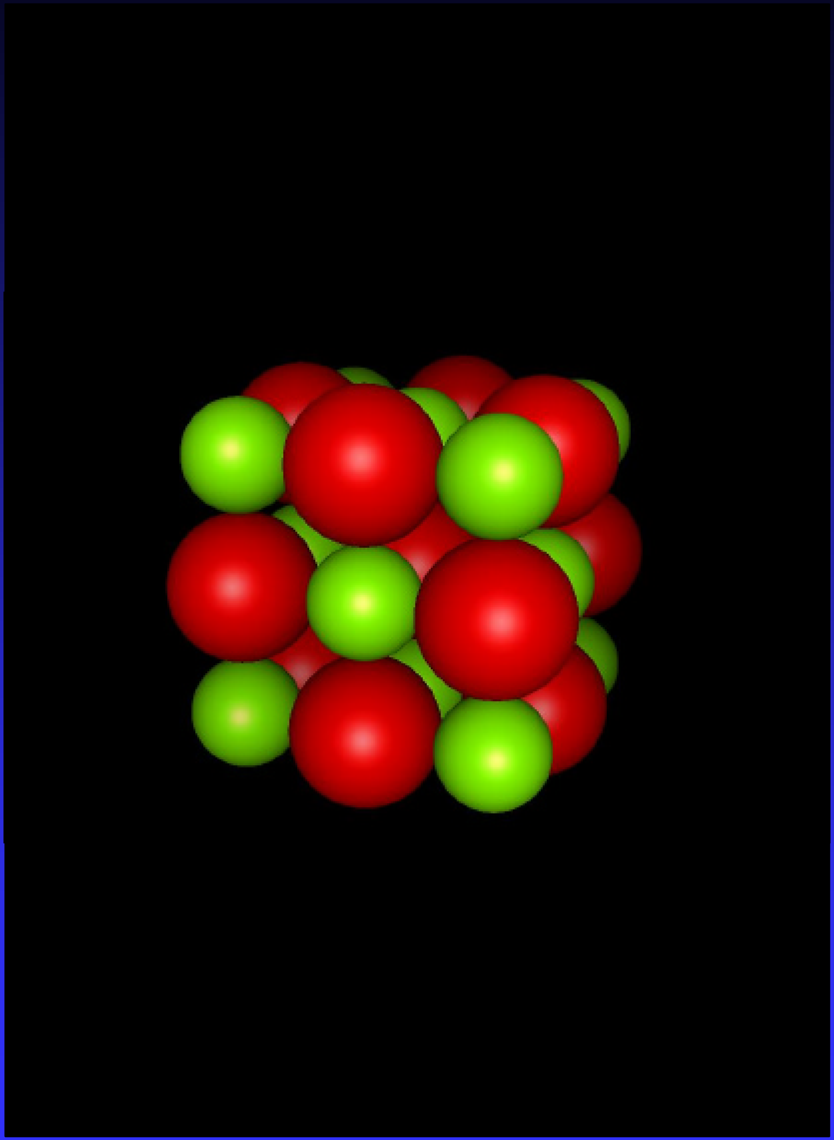
Periclase MgO

Volume (Å^3)	75.69	**74.62**
a(Å)	4.23	**4.21**
b(Å)	4.23	**4.21**
c(Å)	4.23	**4.21**
α	90	**90**
β	90	**90**
γ	90	**90**
Z	4	
ΔE_0 (eV)	- 48.3915	
$\Delta E_0/Z$ (eV)	-12.0979	

Charge population of electronic states suggests prototypical “ionic” lattice: MX

M = Mg^{2+}

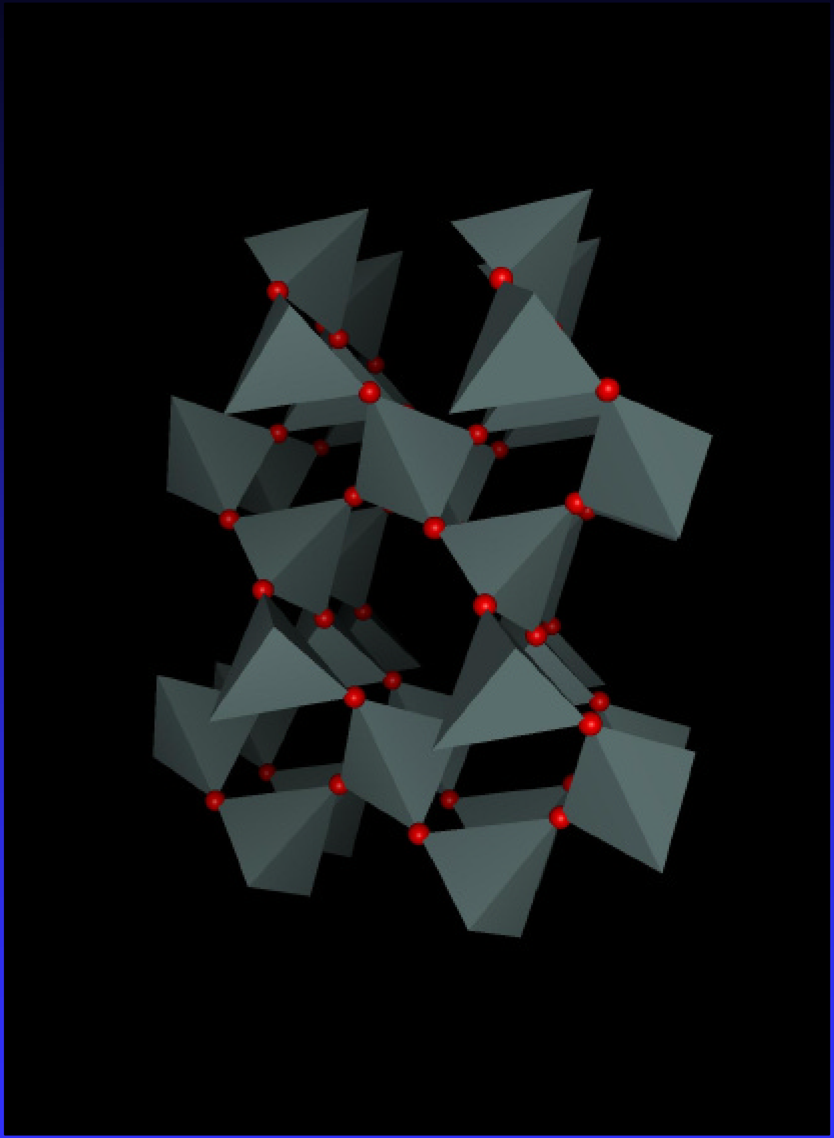
X = O^{2-}



a-**quartz** SiO_2

Volume (Å^3)	118.39	**112.74**
a(Å)	4.99	**4.91**
b(Å)	4.99	**4.91**
c(Å)	5.49	**5.40**
α	90	**90**
β	90	**90**
γ	120	**120**
Z	3	
ΔE_0 (eV)	-71.2139	
$\Delta E_0/Z$ (eV)	-23.7380	

Corner shared network of SiO_4 units.



…a few gas phase examples:

	$CO_{2(g)}$		$H_2O_{(g)}$	
b(Å)	1.19	**1.16**	0.989	**0.957**
θ(Å)	180	**180**	104.8	**104.5**
ΔE_0 (eV)	-22.1578		-14.0071	

Forsterite Reaction energy (GGA-PAW):

$$\underbrace{\tfrac{1}{2} E[Mg_2SiO_{4(s)}] + E[CO_{2(g)}]}_{\text{reactants}} - \underbrace{E[MgCO_{3(s)}] - \tfrac{1}{2}E[SiO_{2(s)}]}_{\text{products}} \sim 1.04\ \text{eV}\ (99\ \text{kJ/mol})$$

Exp: 95 kJ/mol

Volume change (solids):

$$\frac{V(\text{products})}{V(\text{reactants})} = \frac{V[MgCO_3] + \tfrac{1}{2} V[SiO_2]}{V[Mg_2SiO_4]} = 1.80$$

1.90 Exp

Lizardite Reaction energy (GGA-PAW):

Reactants: $E[Mg_3Si_2O_5(OH)_{4(s)}] + 3\,E[CO_{2(g)}]$ ~ -181.434 eV

Products: $3\,E[MgCO_{3(s)}] + 2\,E[SiO_{2(g)}] + 2\,E[H_2O_{(g)}]$ ~ -182.115 eV

0.681 eV
(64.9 kJ/mol)

Exp: 66 kJ/mol

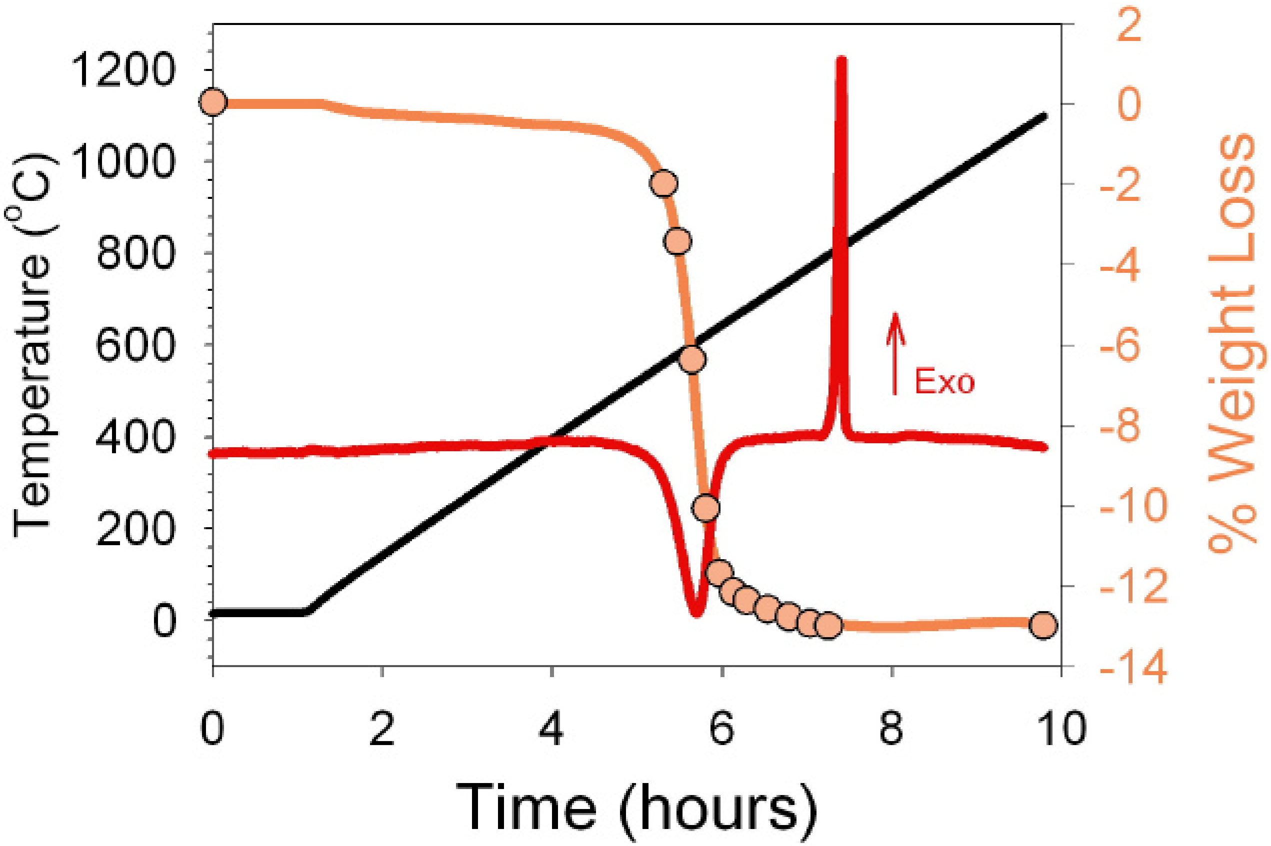
Volume change (solids):

$$\frac{V(\text{products})}{V(\text{reactants})} = \frac{3\,V[MgCO_3] + 2\,V[SiO_2]}{V\,[Mg_3Si_2O_5(OH)_{4(s)}]} = 1.21$$

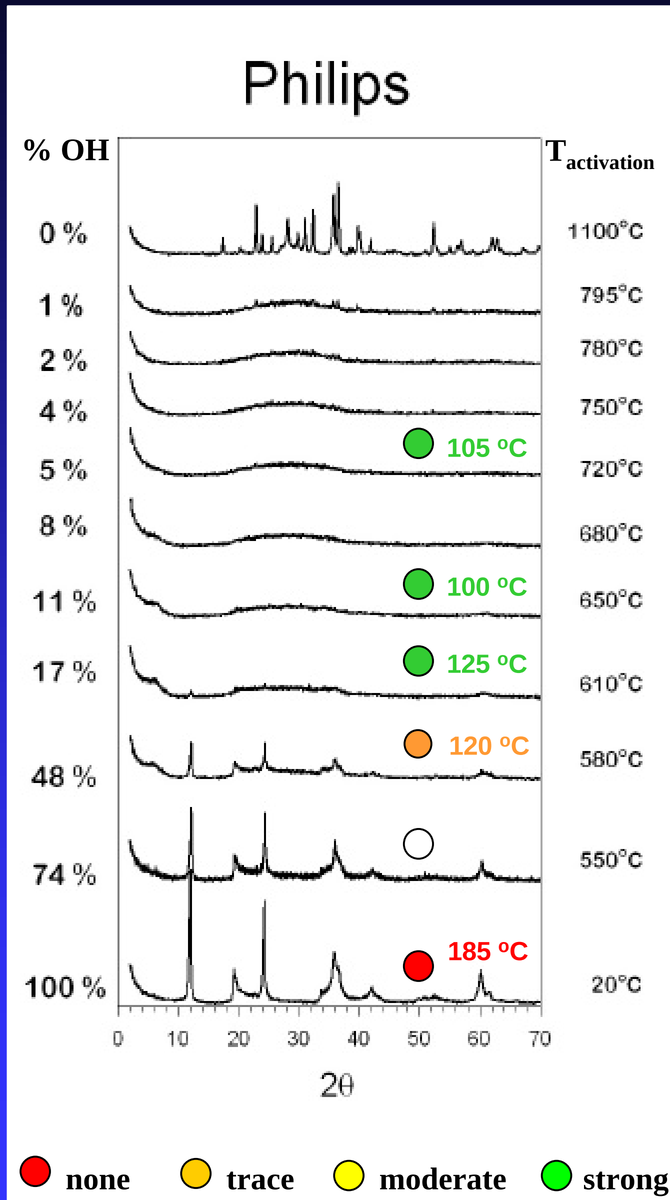
1.17 Exp

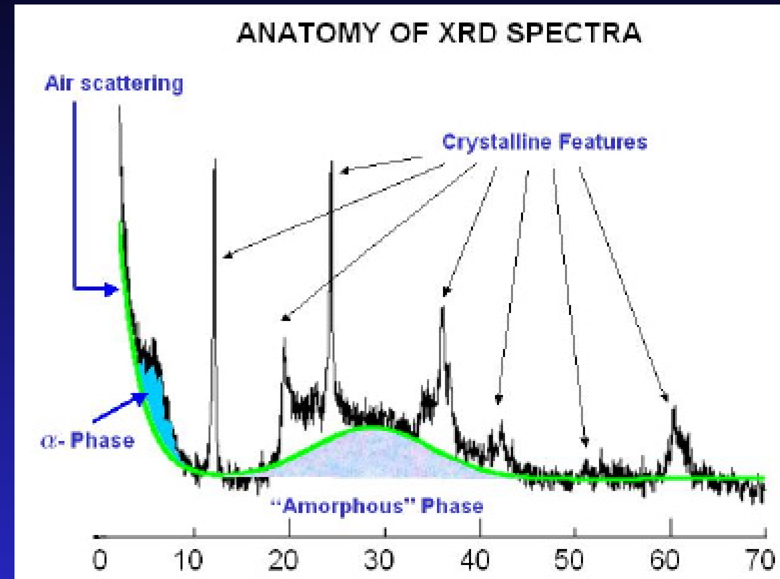
Heat Treatment: Dehydroxylation

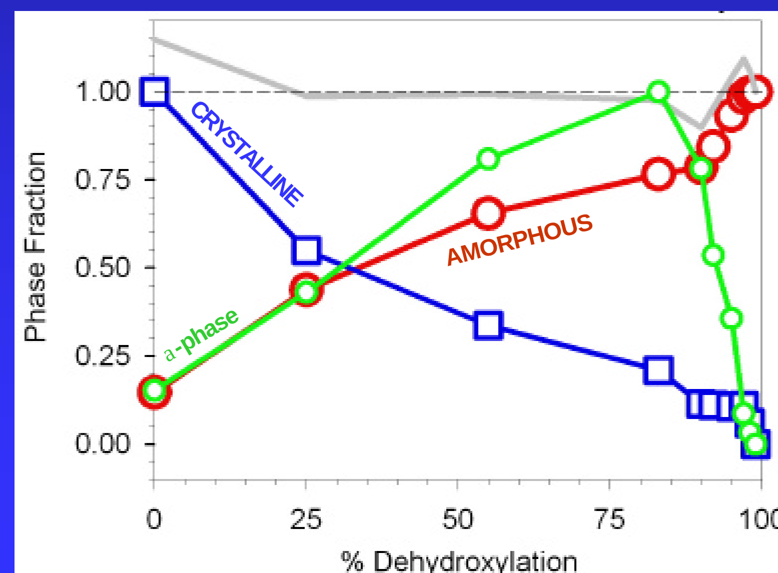
MATERIALS QUENCHED DURING TGA/DTA OF THE LIZARDITE HEAT ACTIVATION PROCESS



MULTIPHASE ANALYSIS OF PHILIPS XRD SEQUENCE

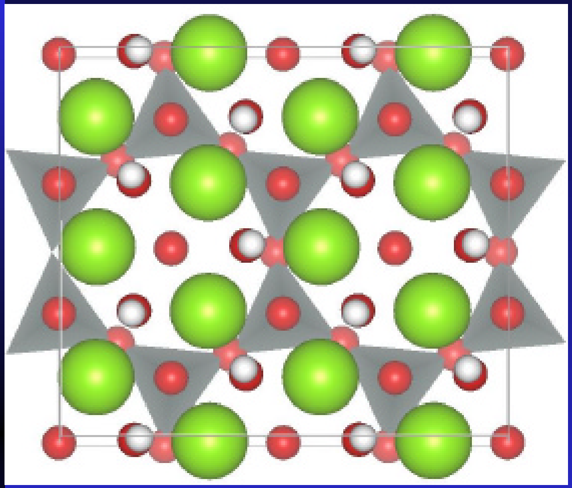






THERMAL DECOMPOSITION MECHANISMS IN 12.5% DEHYDROXYLATED LIZARDITE: STRUTURAL ANALYSIS VIA "DIFFERENTIAL XRD"

View looking down (001)



Objective:

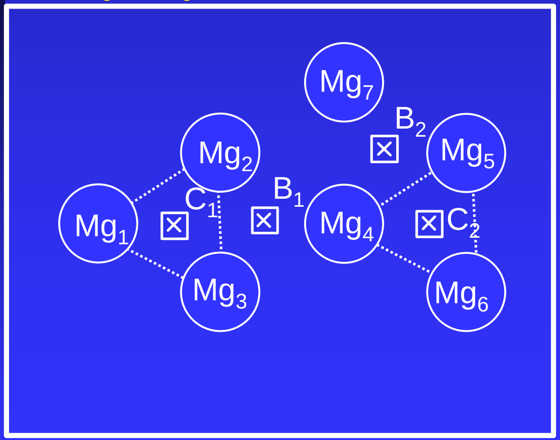
- Long term goal is to understand the structure/morphology of the carbonation reactive meta-serpentine. Build up understanding by looking at the early stages of dehydroxylation first.

Smallest cell possible for 12.5% OH loss

$\rightarrow$ 4 Formula units of 1T-Lizardite:

$$Mg_{12}Si_8O_{20}(OH)_{16} \longrightarrow Mg_{12}Si_8O_{21}(OH)_{14} + H_2O + \Delta E$$

Many ways to choose OH + H



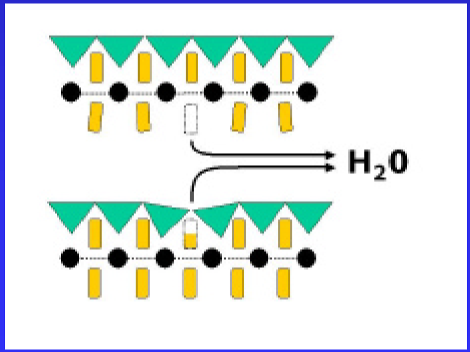
□ Hydroxyl removal site

× Proton removal site

Ab Initio **Prediction:**

Least meta-stable product involves water formation from a "brucite"-layer hydroxyl and a "cage" proton:

$\Delta E \sim +3.5$eV (**81 kcal/mol**) per H_2O removed



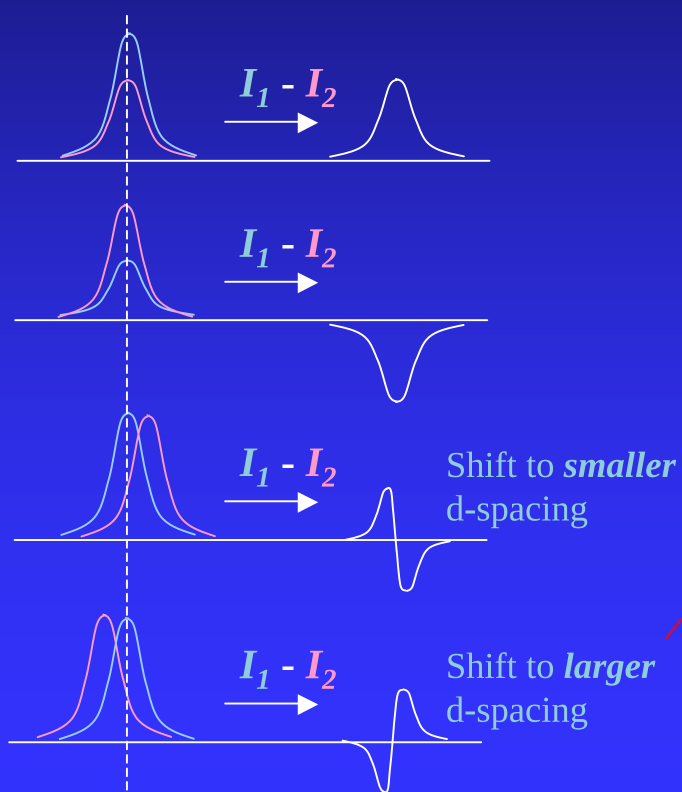
Heteroplanar formation involving "brucite"-layer OH and "cage"-proton favored.

COMPARISON WITH EXPERIMENT: "Differential XRD" Analysis Concept

- Initial dehydroxylation leads to <u>small</u> changes in XRD pattern. Look at difference XRD between 0% and 12.5% dehydroxylated lizardite.

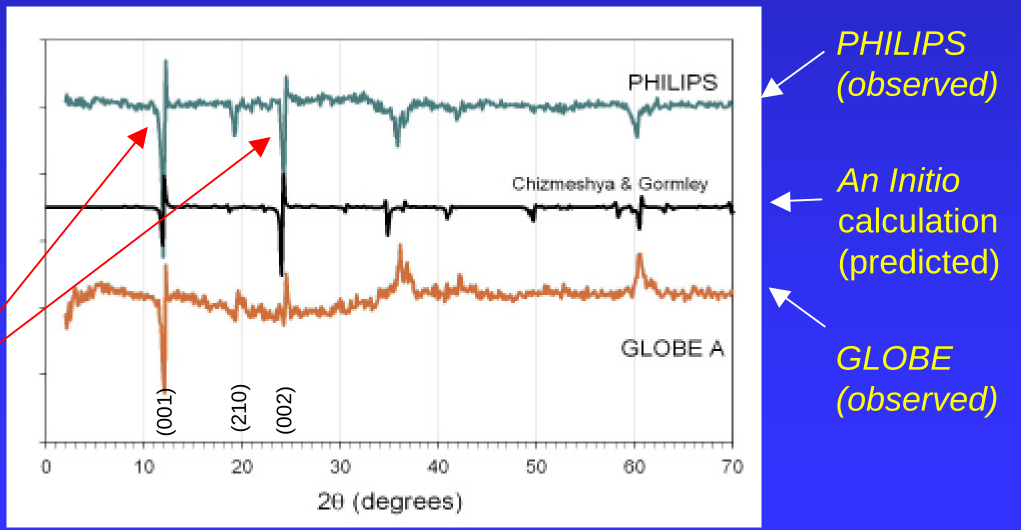
	$a=2a_L$	$b=\sqrt{3}\,a_L/2$	$c=c_L$
100% OH:	10.780	9.359	7.253
87.5% OH:	10.787	9.378	7.238
	0.0 %	**+0.2 %**	**-0.2 %**

- Use *ab initio* simulation to predict the magnitude and sign of the XRD shits.

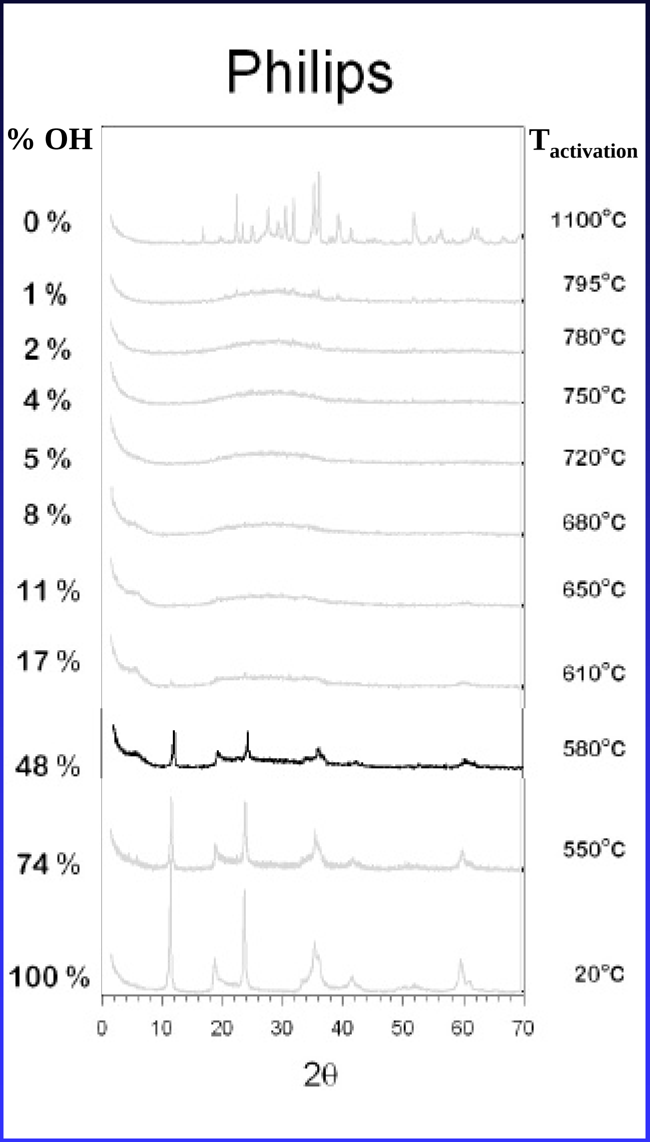


- Magnitudes and positions of differential signatures are ***reproducible***, and correlate well with the *small* chemical and structural differences between the two samples.

XRD Difference for (*Philips-550 ºC*)-(*Philips-20 ºC*)



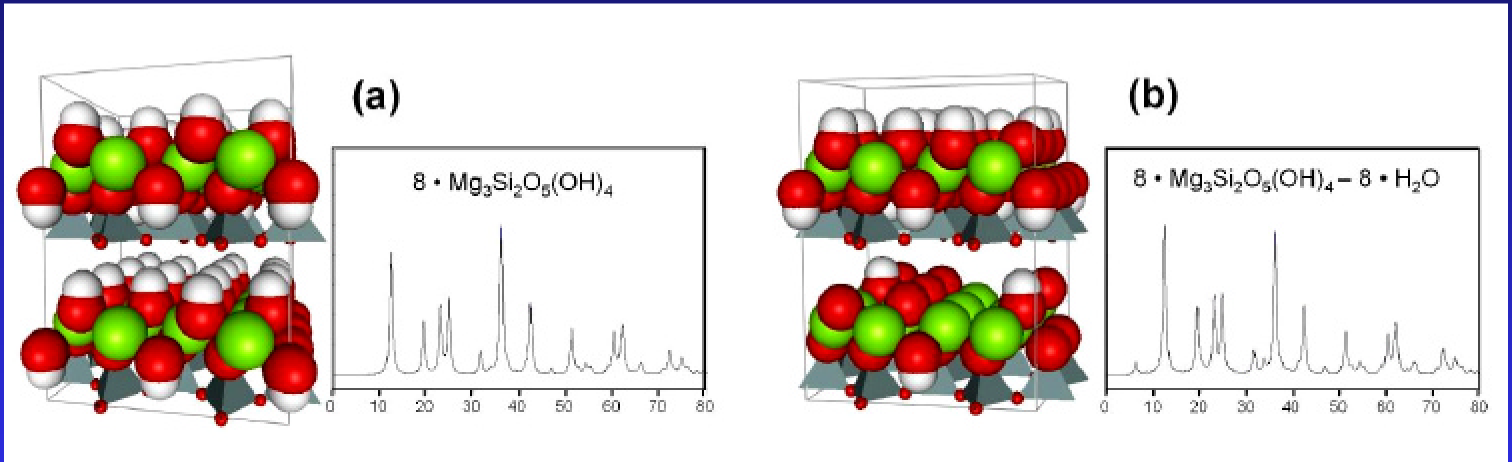
MODELING 50% dehydroxylated meta-serpentine



MODELING 50% dehydroxylated meta-serpentine

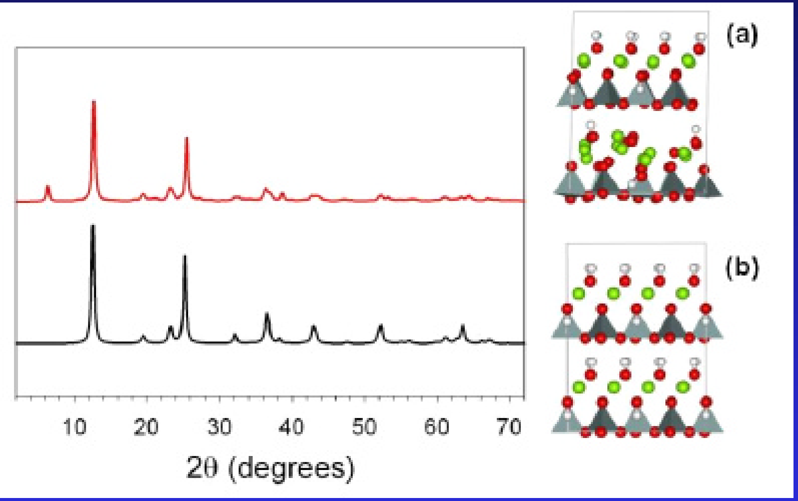
- Construct several dozen 144-atom lizardite cells and remove (*via* hetero- or homo-planar removal) 50% water → $8 \cdot Mg_3Si_2O_5(OH)_4 - 8 \cdot H_2O$

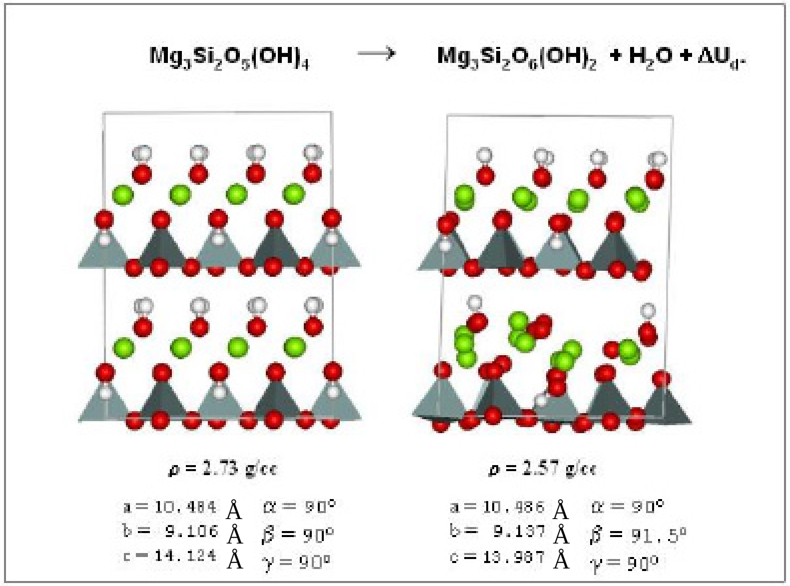
- Low-angle (~6°) XRD feature can only be reproduced when hydroxyls preferentially dissociate from alternating layers *with a ratio of 4:1 or greater*.



MODELING 50% dehydroxylated meta-serpentine

- Construct several dozen 144-atom lizardite cells and remove (*via* hetero- or homo-planar removal) 50% water → $8 \cdot Mg_3Si_2O_5(OH)_4 - 8 \cdot H_2O$
- Low-angle (~6°) XRD feature can only be reproduced when hydroxyls preferentially dissociate from alternating layers *with a ratio of 4:1 or greater*.



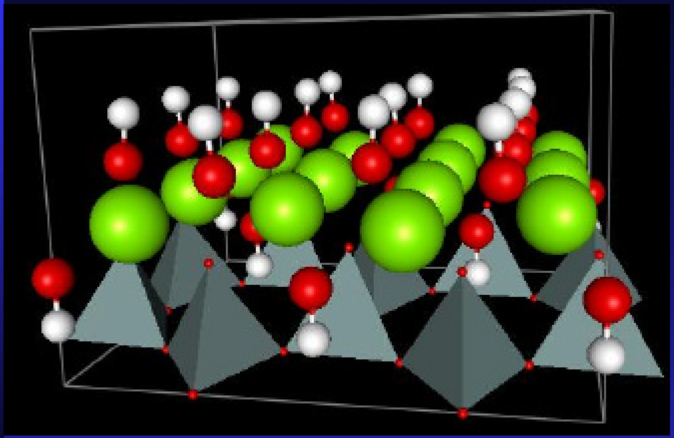


ΔU_d ~ **+2.9** eV per H_2O *(c.f. **+3.5** eV per H_2O for 12.5% dehydrox model)*

…are these structures dynamically stable?
What is the dehydroxylation *mechanism*?

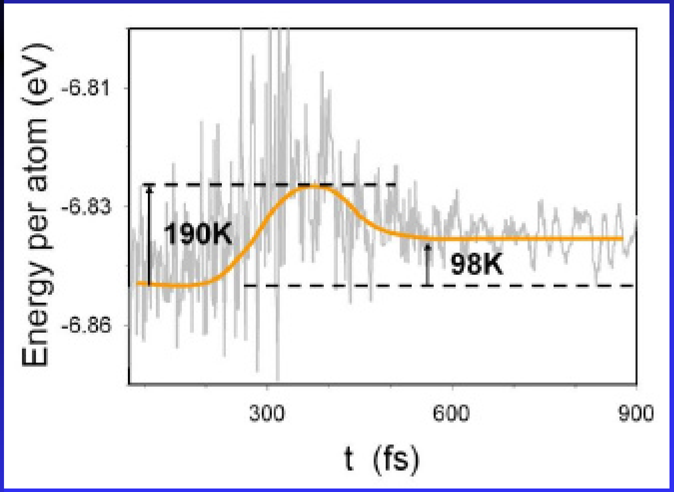
Dynamical Simulations at Finite Temperature

300K SIMULATIONS OF LIZARDITE



Simulation Conditions:

- 72 to 144-atom cells (as in earlier dehydroxylation calculations).
- 1.5 femtosecond timestep integration using the Verlet algorithm
- Local density approximation (LDA)
- Ultra-soft pseudopotentials used to replace core electrons.
- Electronic structure computed (using the VASP code) at every time step + velocity rescaling.



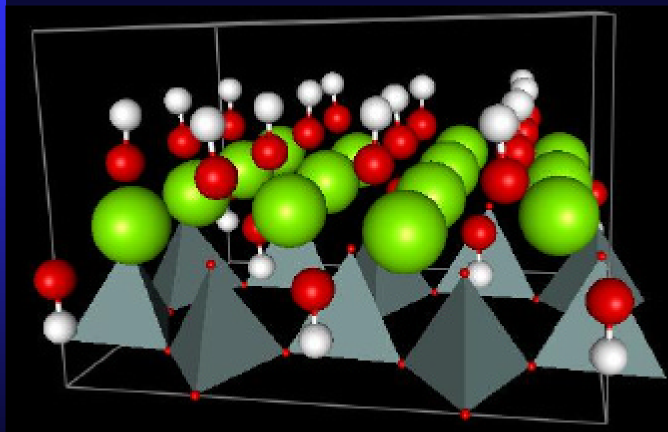
Interpretation:

- Slightly metastable (β) phase predicted at room temperature.
- Inverted hydroxyl within the brucite layer
- High quality static lattice calculations →

Primitive unit cell: lizardite a = 5.265 Å
c = 7.090 Å
E = 0.

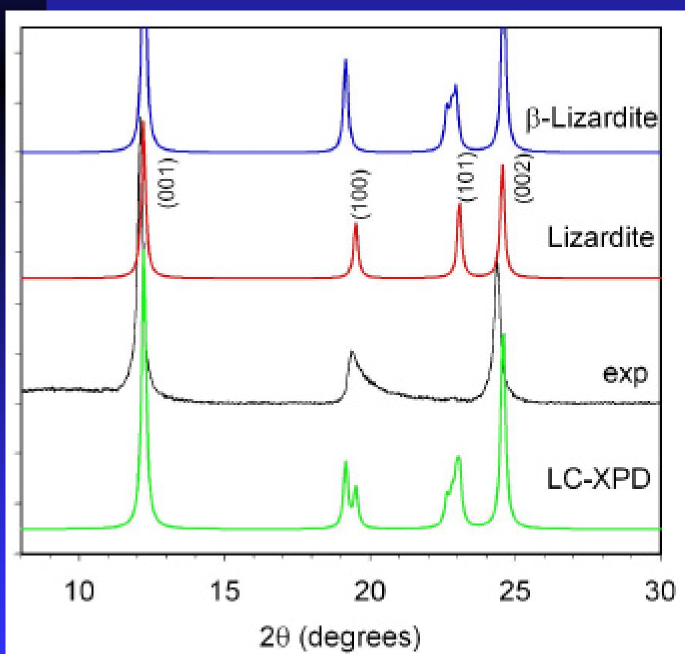
β-lizardite a = 5.344 Å
c = 7.092 Å
E = 0.021 eV/atom

300K SIMULATIONS OF LIZARDITE



Simulation Conditions:

- 72 to 144-atom cells (as in earlier dehydroxylation calculations).
- 1.5 femtosecond timestep integration using the Verlet algorithm
- Local density approximation (LDA)
- Ultra-soft pseudopotentials used to replace core electrons.
- Electronic structure computed (using the VASP code) at every time step + velocity rescaling.

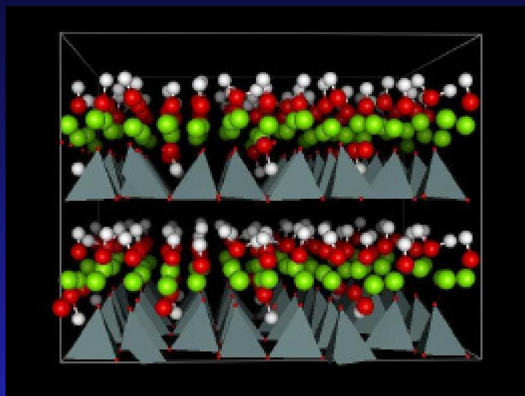


Implications for XPD and IR:

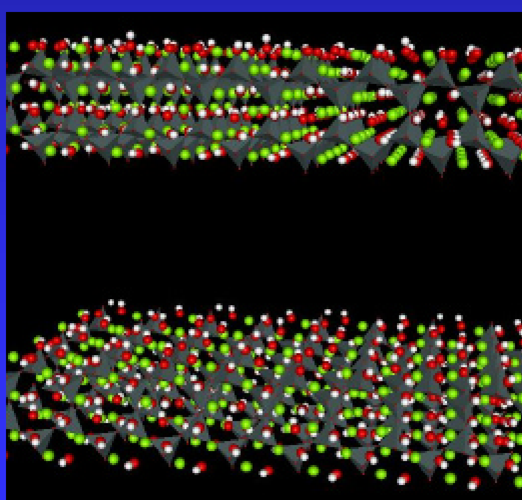
- Origin for unexplained splittings and asymmetry of various in-plane features? E.g. (100) and (101)?
- Origin of the unexplained high frequency shoulder on the OH bands. Calculations in progress.
- Must examine distributions of inverted hydroxyl configurations at 300K.

* Preferred orientation not included…

HIGH-TEMPERATURE DYNAMICAL SIMULATIONS OF LIZARDITE & META-LIZARDITE



Bulk lizardite @ 1000K



Free surface (11$\bar{2}$0) @ 1000K

Objectives:

- Use state-of-the-art quantum simulation to study the dynamics of protons/hydroxyls as a function of temperature.
- Diffusion of H, OH, H_2O – stability of silica sheets.
- Identify dehydroxylation path/mechanism…

Simulation Conditions:

- 72 to 144-atom cells (as in earlier dehydroxylation calculations).
- 1.5 femtosecond timestep integration using the Verlet algorithm
- Local density approximation (LDA)
- Ultra-soft pseudopotentials used to replace core electrons.
- Electronic structure computed (using the VASP code) at every time step + velocity rescaling.

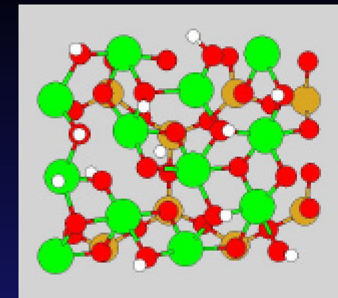
Interpretation:

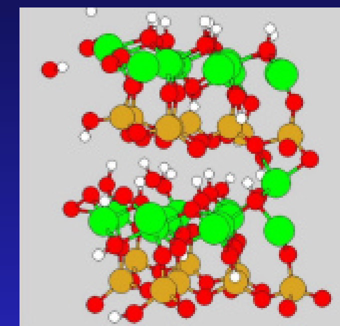
- Significant proton diffusion found for protons in “cage” sites (e.g., within silica sheet).

- Silica layers remain integral on a long time scale compared to the proton hopping rate between cage sites.

- Frequent formation of meta-stable water within brucite layers in the bulk crystal (simulations underway to determine this rate via transition state theory). Proton diffusivity significantly enhanced near the surface.

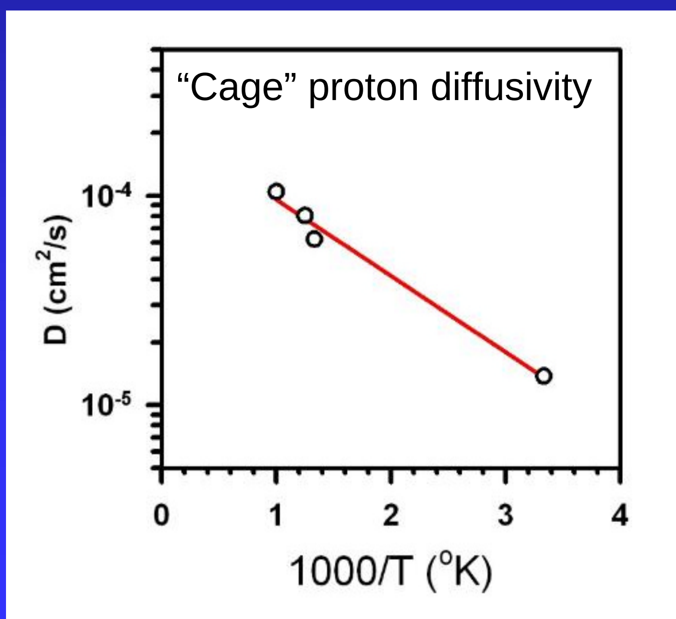
DIFFUSIVITIES: $\langle |r_i(t)-r_i(0)|^2 \rangle_N = 6Dt$





D ($\times 10^{-5}$ cm^2/s) @ T = 1000ºK (~700ºC)

Species	Bulk Environment	$(11\bar{2}0)$ Surface	
"Brucite" protons	10.2	22.8	x 2
"Cage" protons	10.3	20.3	
Magnesium	0.07	0.30	**x 4**
Silicon	0.05	0.10	x 2
"Cage" oxygens	0.06	0.97	**x 16**
Other oxygens	0.06	0.19	x 3

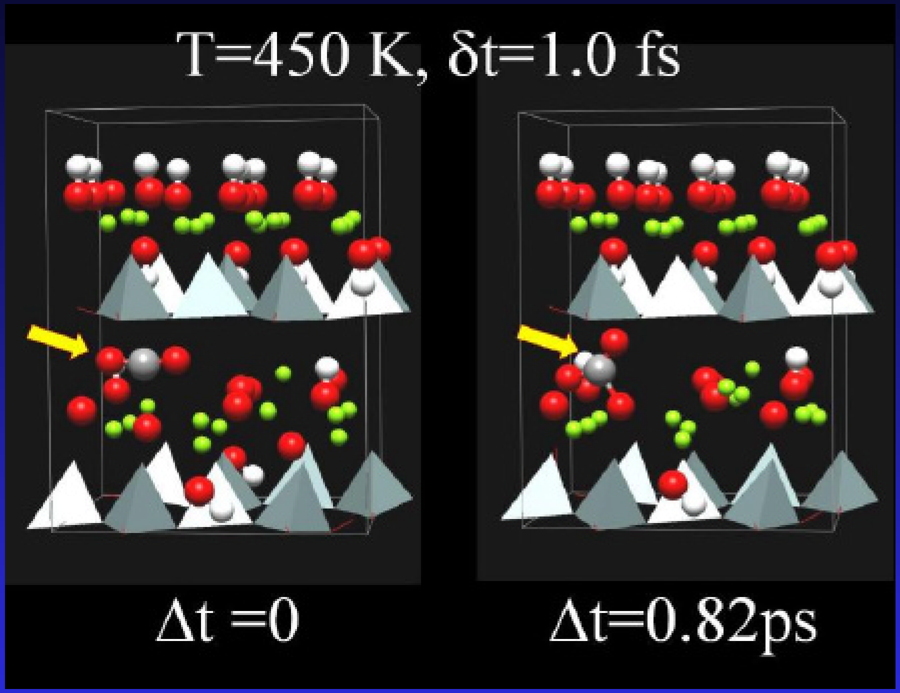


72-atom bulk lizardite runs at 300, 750, 875, 1000ºK.

Interpretation:

- **SURFACE:** High diffusivity of "cage" protons and oxygens promotes water formation via CB mechamism
- **BULK:** Water formation likely dominated by BC mechanism.
- Thermal activation energy for bulk proton is diffusion is very small, ~ 10kJ/mol (→ RT effects like OH inversion…)
- Repeat these calculations for dehydroxylated models to study dissolution.

SOLID PHASE CARBONATION PROCESS IN META-LIZARDITE:



Objective:

The open “pillared” configuration of meta-lizardite may permit direct reaction of CO_2 with the mineral under the supercritical conditions. What are the active sites in meta-lizardite?

Simulation Conditions:

- 144-atom cells, T=450ºK
- t=1.0 fs integration using the Verlet algorithm
- Local density approximation (LDA)
- Ultra-soft pseudopotentials used to replace core electrons.

Outcome:

- Open structure supported by OH “pillars” stable on long timescale. Silica sheets remain a rigid network.
- Binding energy ~ 2.82 eV (65 kcal/mol) per CO_2. Active sites are low coordination oxygens within disrupted hydroxyl layer.
- CO_2 forms carbonate “propeller” structure.
- Dissolution of these carbonate units could provide a supply of precursors for aqueous growth…

Aqueous Solution

Equilibrium Solution: Na buffered H_2O-CO_2

Q: Given P_{CO2}, [Na+] and T what are $[CO_2]$ $[OH^-]$ $[HCO_3^-]$ $[CO_3^{2-}]$ and $[H^+]$

A: Solve the following equation:

$$CO_{2(g)} \rightarrow CO_{2(aq)} \quad ; K_H = \frac{[CO_2]}{\gamma_{CO2}\, P_{CO2}}$$

$$CO_{2(aq)} + H_2O \rightarrow H^+ + HCO_3^- \quad ; K_1 = [HCO_3^-][H^+]/[CO_2]$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \quad ; K_2 = [H^+][CO_3^{2-}]/[HCO_3^-]$$

$$H_2O \rightarrow H^+ + OH^- \quad ; K_W = [H^+][OH^-]$$

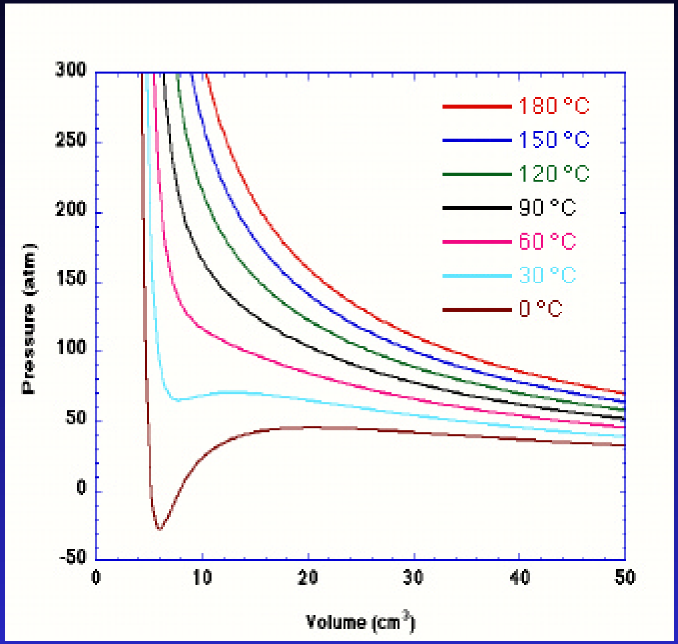
$$Na^+ + H_2O \rightarrow NaOH^- + H^+ \quad ; K_{Na} = [H^+][OH^-]$$

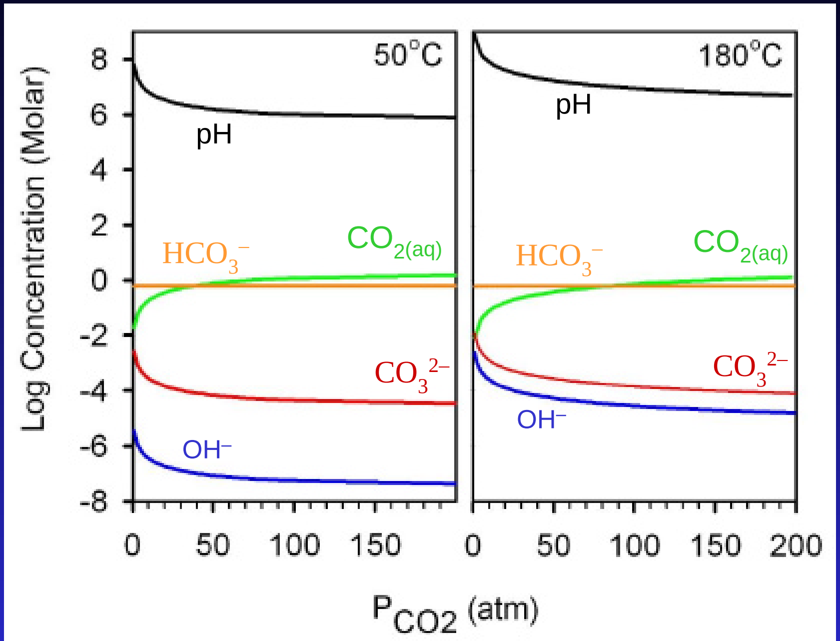
$$[Na^+] + [H^+] = [OH^-] + [HCO_3^-] + 2\,[CO_3^{2-}]$$

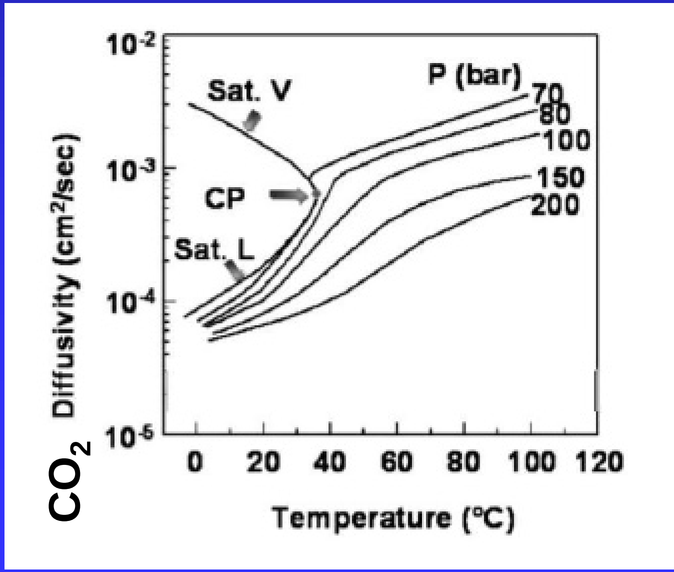
Systematic improvements:

- Use T-dependent equilibrium constants
  (W. Stumm and J.J. Morgan *Aquatic Chemistry*. 3rd Ed., John Wiley & Sons, (1995).
- Use an appropriate, high-quality equation of state for CO_2 to obtain γ_{CO2} (Z.H. Duan and R. Sun, *Chem.Geo.* **193** (3-4): 257-271 (2003)

Equilibrium Solution: Na buffered H_2O-CO_2 $[Na^+]=0.64$







- Diffusivity information for other species is very limited.
- The thermodynamics of the CO_2-H_2O in the presence of solutes is a difficult problem (many key parameters unknown)
- Can the effect of other buffer ions on CO_2-H_2O fluid thermodynamics be predicted reliably? (e.g. Li)

Neil R. Foster, 2002 Eiffel Corporation

Quantum Mechanical Modeling of Solution Chemistry

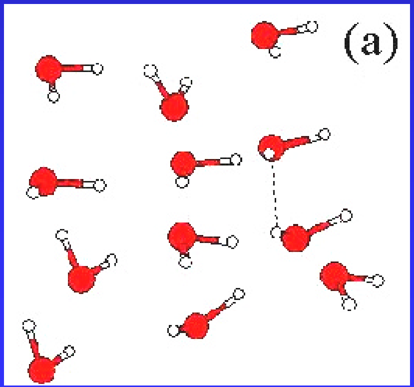
Why turn to Quantum Modeling?

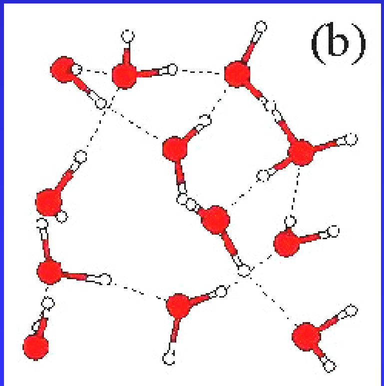
Some things are hard to measure: "local" pH, true speciation, diffusivities, excess free energy & general properties of dense liquid phases

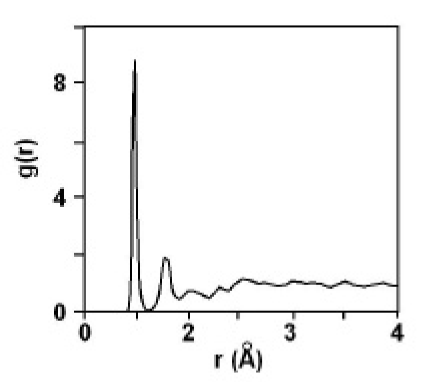
Classical potential simulations: not quantitative, many fitting parameters, no bond breaking, polarizability missing…

Brute force Quantum Molecular Dynamics?

…possible, but need vast resources to do even small systems properly







[48 H2O molecule simulations performed using PAW-GGA based VASP DFT code]

Timescales: ~ ps
Length scales: ~ nm

10 ps run:

$<|r_i(t)-r_i(0)|^2>=6Dt$

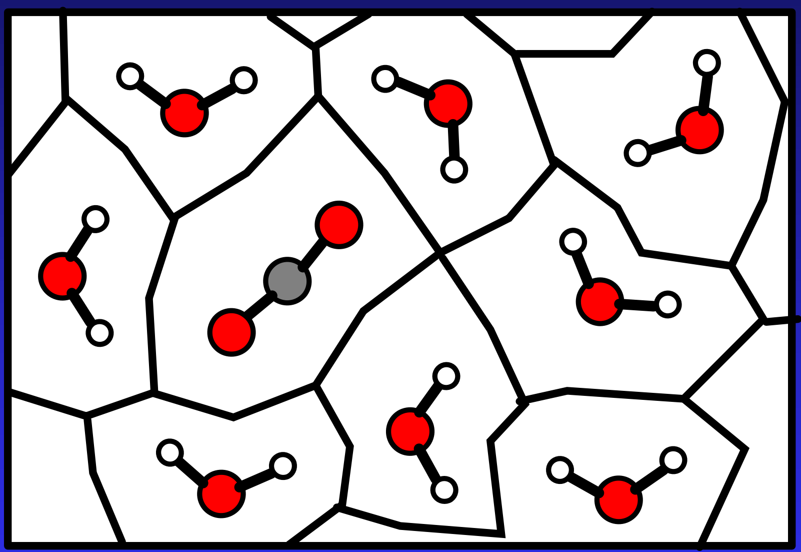
D ~ 2.9×10^{-5} cm^2/s

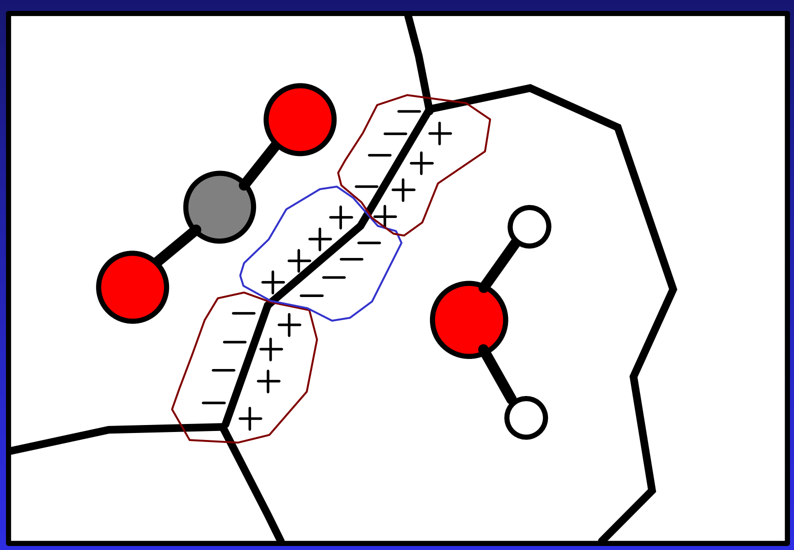
(D_{exp} ~ 2.5×10^{-5} cm^2/s)

COSMO-RS [A. Klamt, V. Jonas, J. Phys. Chem. **99**, 2224 (1995)]

(Conductor-like screening model for Real Solvents)

- Molecular placed within a conforming cavity.
- Screening charge density calculated accurately for each solute on cavity surface.
- Contact interactions between surfaces given in terms of induced charge distributions
- Slightly more effort than gas phase *ab initio* molecular calculations



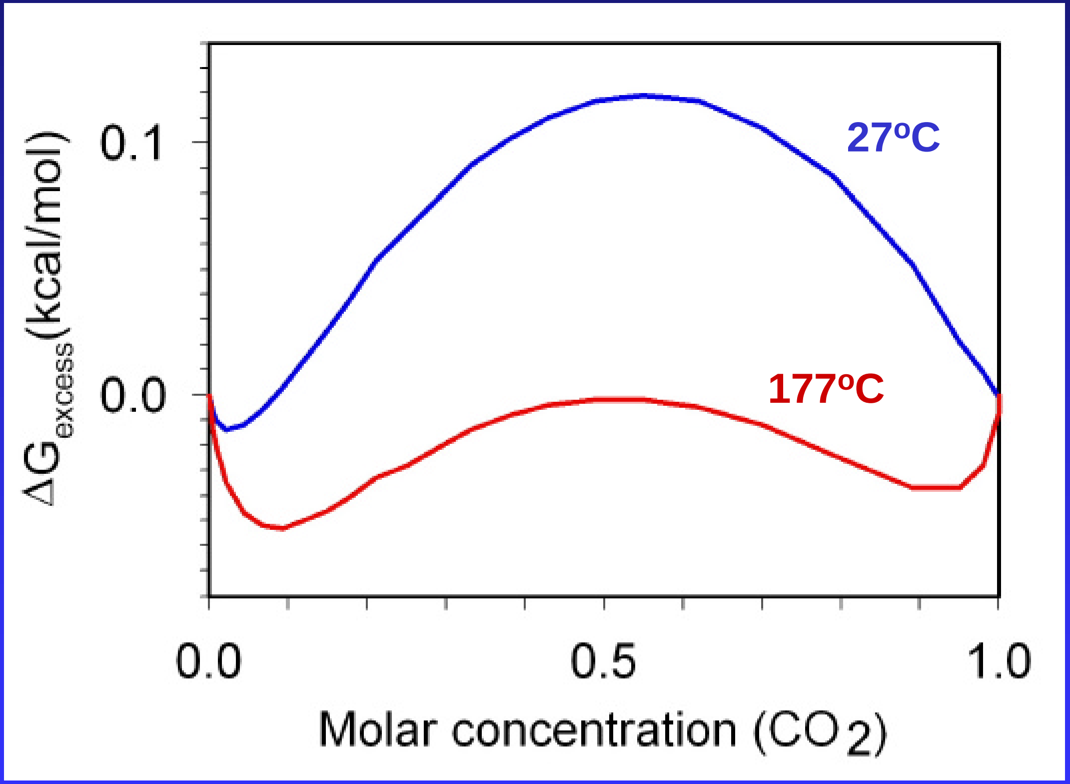


Advantages: solvents and solutes treated on the same footing
accurate density functional theory can be used for electronic structure

Predicted quantities: $\Delta G_{hydration}$, vapor pressures, heats of mixing, miscibility gaps, excess free energies...

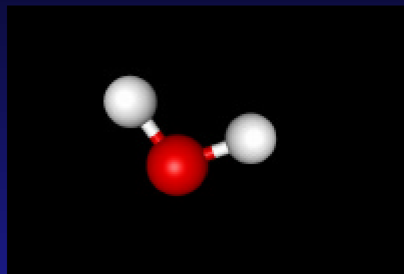
COSMO-RS Procedure:

1) Put molecules into “virtual” conductor
2) Compute electronic/structural properties of molecules using DFT
3) Compress the ensemble to desired density
4) Remove the conductor on molecular contact areas
5) Compute thermodynamic properties…



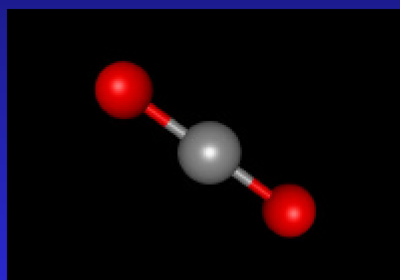
Solvation Induced Spectroscopic Shifts:

(COSMO-RS Calculations using DMol3, DNP Basis and PW91 GGA)



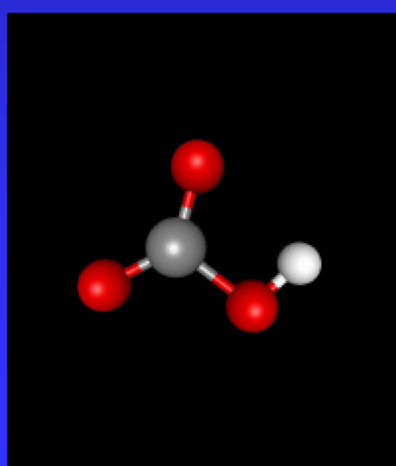
H_2O(aq)	H_2O(g)	Dw(cm^{-1})	
1593.3	1599.2	–5.9	bend
3698.6	3712.7	–14.1	sym str.
3802.8	3829.9	–27.1	asym str →

Experiment → ~ –40-80 cm^{-1}
Shifts in asym. Str. mode



CO_2(aq)	CO_2(g)	Dw(cm^{-1})	
617.4	626.2	–8.8	bend
618.3	626.2	–7.9	bend
1335.5	1321.1	+14.4	sym str.
2328.8	2349.1	–20.3	asym str.

Degeneracy is lifted:
Experiment → ~ 10 cm^{-1}
(S.G. Kazarian et al.,
Chem. Commun.,2047,2000)



HCO_3^-(aq)	HCO_3^-(g)	Dw(cm^{-1})	
533.6	523.9	+9.7	
541.8	582.6	–40.8 ←	hydroxyl wagging
629.3	590.7	–38.6 ←	hydroxyl wagging
792.6	779	+13.6	
862.5	**819**	+43.5 ←	C-(OH) stretch
1171.1	1167.1	+4.0	
1276.9	1271.6	+5.3	
1663.2	**1749.6**	–86.4 ←	“Asym.O-C-O stretch”-like
3673.8	3670.9	+2.9	

Implications:

Conventional X-ray and EXAFS are poor probes of the liquid state since C and O atoms of the carbonate species are not distinguishable from the O atoms in H_2O.

Infrared spectroscopy *could* be used to monitor the concentrations of aqueous species, however:

- Absorption depends on speciation, but also on pressure, ionic strength, etc.

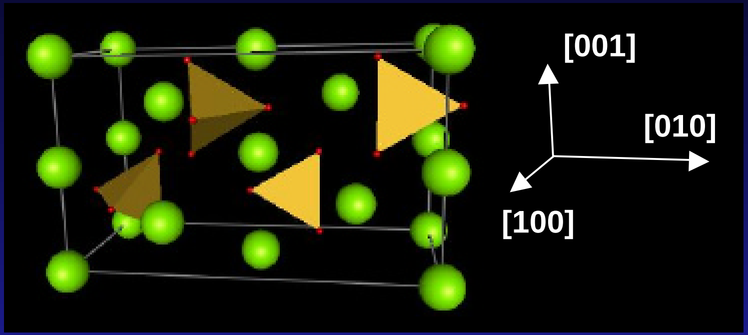
How about NMR?

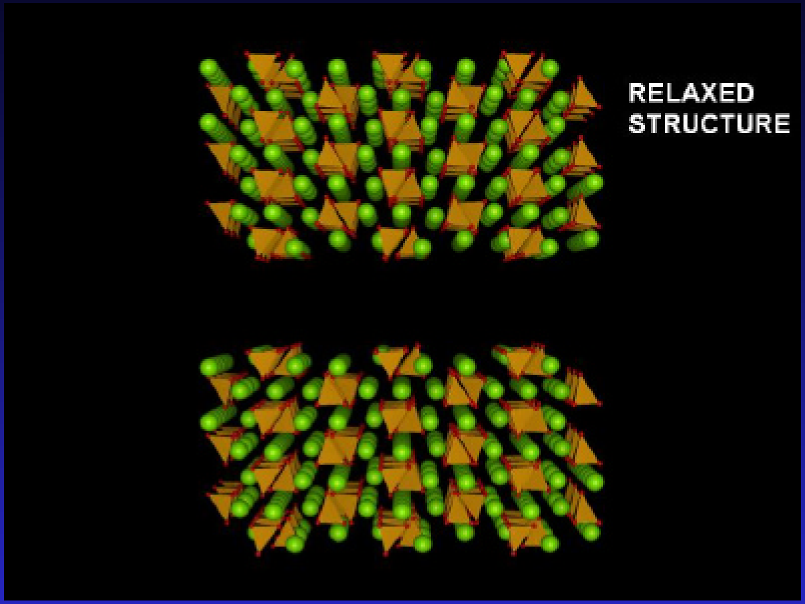
- superior sensitivity
- chemical shifts directly proportional to concentration

Surface Physics/Chemistry

SURFACE PROPERTIES OF OLIVINE VIA SIMULATION

Unit cell of Mg_2SiO_4:





Objective:

- Explore relationship between surface structure and dissolution. Is there a face dependence? How do different surfaces reconstruct/relax?

- Carry out simulation studies to help interpret complementary surface facet/reactivity studies.

Ab Initio Modeling:

- Build symmetrical multi-layer slabs from unit cells. Lateral slab dimensions based on bulk geometry.

- Tested 3-, 5-, and 7-Mg layer geometries.

- Built slabs with (100), (010) and (001) surface normals.

- Forces on all atoms minimized using accurate quantum mechanical approach (VASP code).

Outcome:

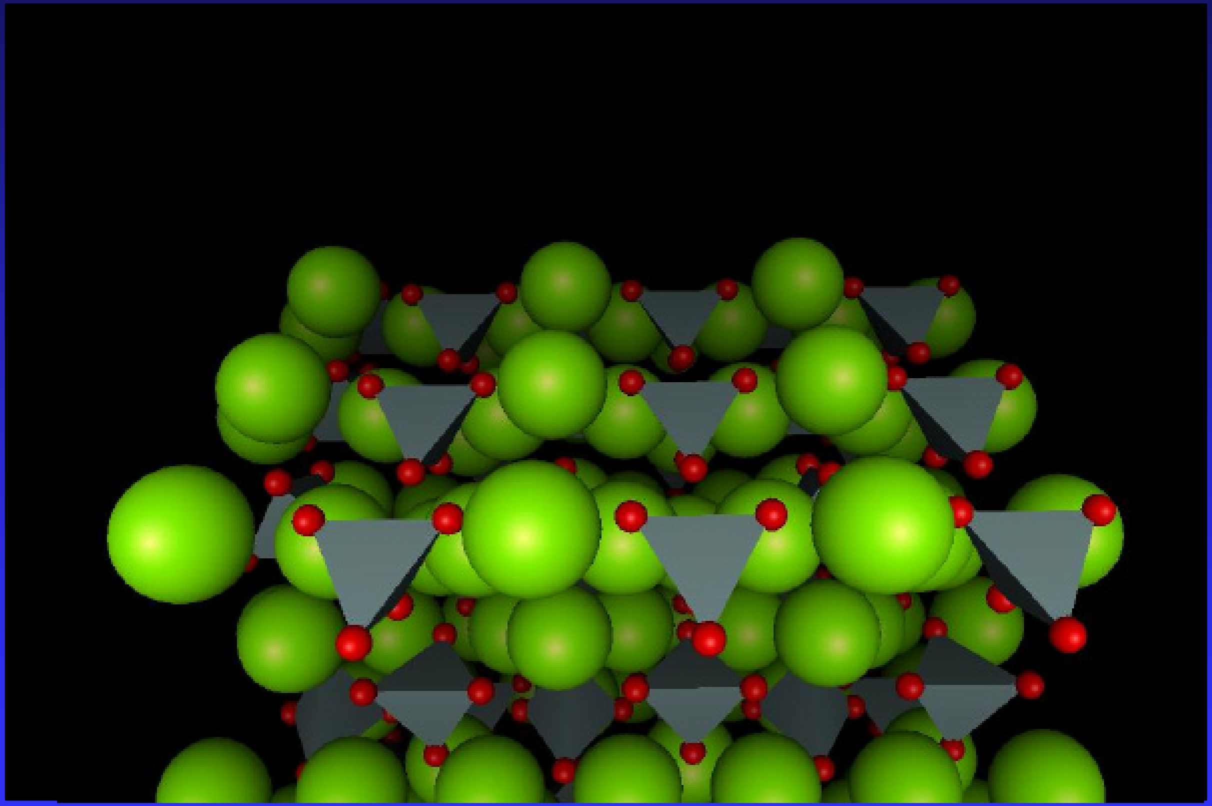
- Large scale reconstruction is found for the (100) surface (shown above), extending 3 “silica” layers down. Minimal reconstruction found for (010) and (001) surfaces. Tetrahedral tilt hindered in the latter.

- Predict row doubling reconstruction parallel to (001) axis involving SiO_4 units and Mg ions moving out of phase.

- Exposure of magnesium ion rows parallel to (001) axis may provide easy route for dissolution…but next layer requires incongruent dissolution…(010) is best.

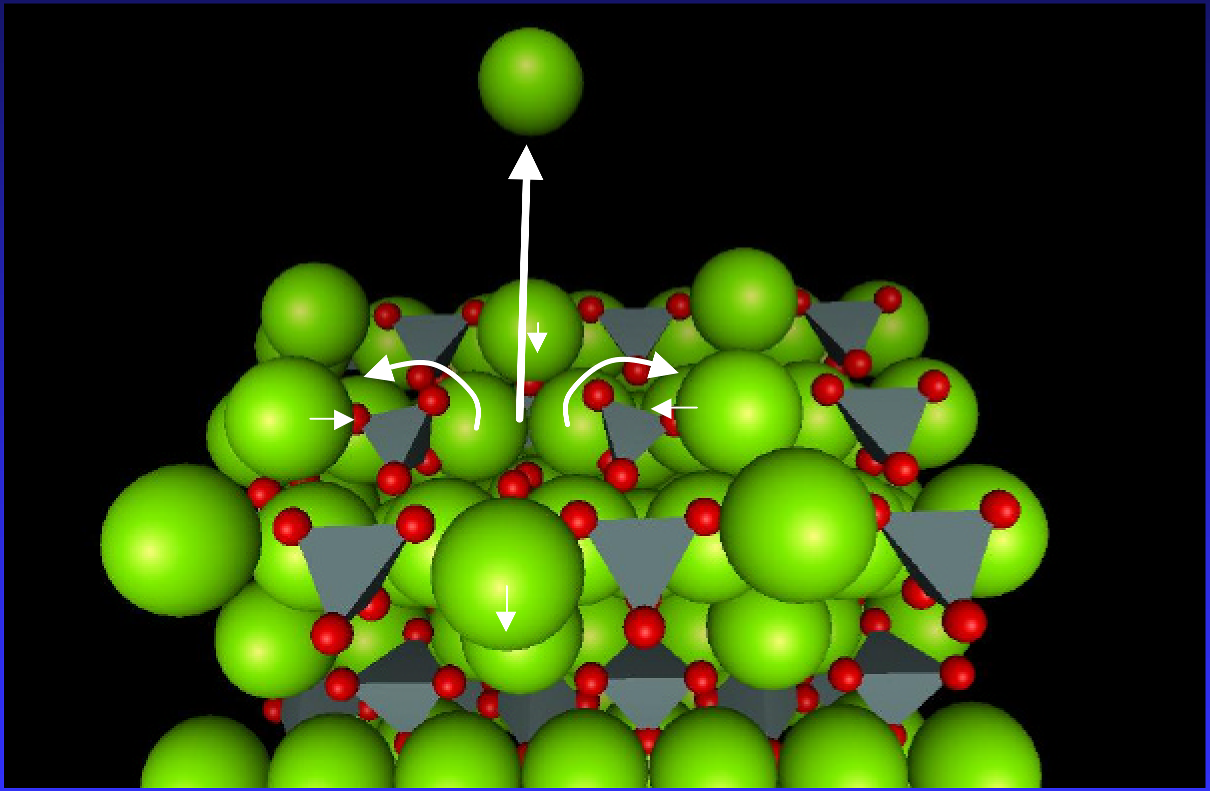
First step in Mg dissolution…

- Minimum dipole surface (010)



First step in Mg dissolution…

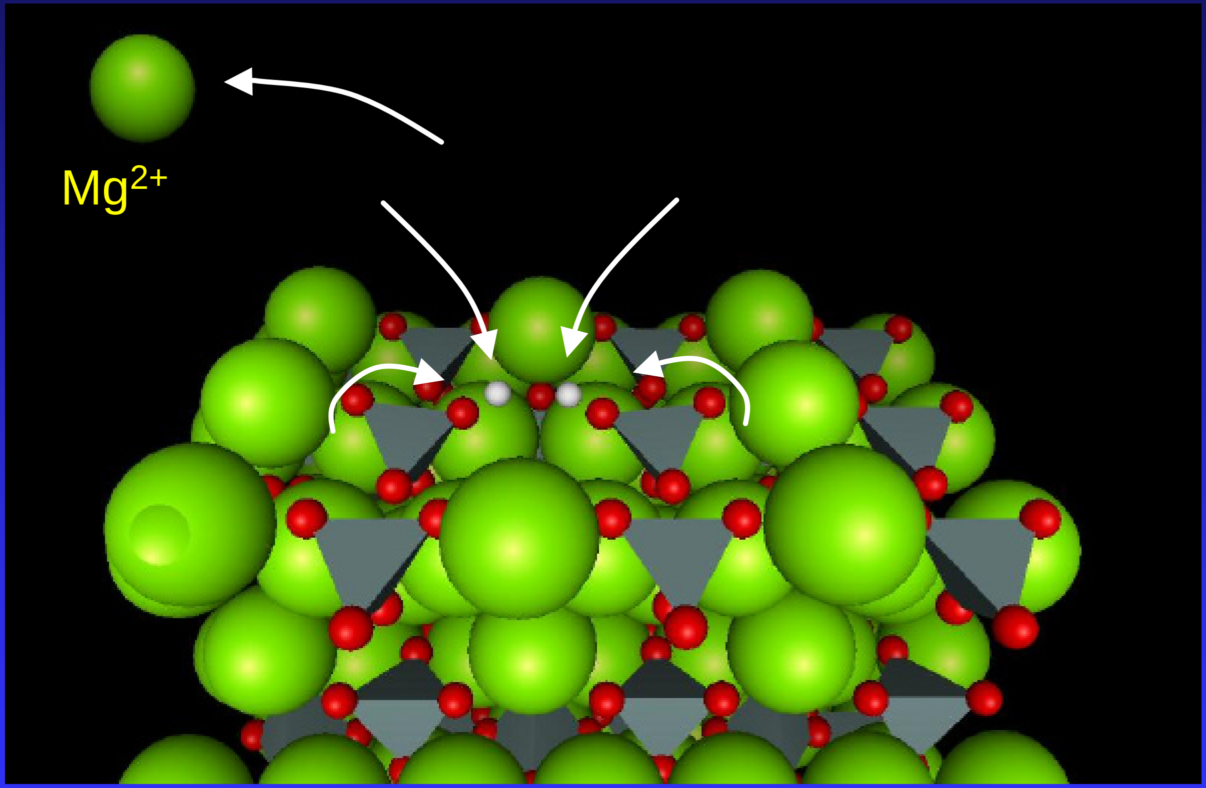
- Minimum dipole surface (010) → Straight removal of Mg^{2+}
  $\Delta E \sim 48$ kcal/mol (endothermic)



First step in Mg dissolution…

- Minimum dipole surface (010): 2 $H^+ \longleftrightarrow Mg^{2+}$ at M2 sites

  ΔE ~ -75 kcal/mol (exothermic)



Analogous results for Fe?

2 $H^+ \leftrightarrow Fe^{2+}$ at M2 sites

DE ~ -55 kcal/mol

…less favorable than Mg^{2+}.

Complexation?

Reactant-product state barrier calculation using NEB in progress…
…estimate prefactor from thermo, QM simulation → activation energy.

Conclusions:

- First principles predictions of solid phase properties are systematic and reliable.
- Simulations indicate that dehydroxylation is extremely complex. Stable structures exhibiting staging behavior are predicted. Silica sheets exhibit stability at high T. Large proton diffusivities are present over a broad temperature range → many paths to dehydroxylation.
- Once lizardite is decomposed, highly reactive low-coordination oxygen sites readily "carbonate" (ΔE = -65 kcal/mol)…
- COSMO-RS method for computing solution properties explored for CO_2-H_2O. Predicts exsolution: CO_2-rich and H_2O-rich fluid phases… **Future work:** Extension and Validation to 3- and 4- component fluids.
- Solvent effects on structural and vibrational properties of solutes reasonably well predicted by the COSMO-RS method → suggests spectroscopic approach to solution characterization feasible: FTIR or NMR spectroscopy
- Minimum dipole Forsterite surface predicted to be (010), large structural reconstruction on (100), less so on (001). **Future work:** Mobility of Fe near surface…
- Proton exchange reaction (dissolution on (010) surface) is predicted to be exothermic by ~ 75 kcal/mol, but ~ 55 kcal/mol for Fe. **Future work:** Reaction Rates from "Nudged Elastic Band" method…